

Pure Shift Nuclear Magnetic Resonance: a new tool for plant metabolomics.

Juan M. Lopez¹, Vanessa Leyva¹, Helena Maruenda¹

¹Departamento de Ciencias – Química, CERMN, Pontificia Universidad Católica del Perú

Correspondence to: Juan M. Lopez at juan.lopez@pucp.edu.pe, Helena Maruenda at hmaruen@pucp.edu.pe

SUPPORTING FIGURES:

The screenshot displays the Bruker TopSpin 3.2 software interface, specifically the 'AcquPars' (Acquisition Parameters) window. The window is titled 'AGVIII-82-1C 5001 1 C:\Bruker\TopSpin3.2\data\HM-2020\nmr'. The 'AcquPars' tab is selected, showing various acquisition parameters for a 'CryoProbe'.

Parameter	Value	Description
PULPROG	reset_psyche_1d	Pulse program for acquisition
TD	4096	Time domain size
SWH [Hz, ppm]	5000.00	Sweep width
AQ [sec]	0.4096000	Acquisition time
RG	22.6	Receiver gain
DW [μsec]	100.000	Dwell time
DE [μsec]	18.00	Pre-scan-delay
d0 [sec]	0.00000300	Incremented delay (2D) [3 usec]
D1 [sec]	2.000000000	Relaxation delay; 1-5 * T1
d11 [sec]	0.03000000	Delay for disk I/O [30 msec]
d12 [sec]	0.00002000	Delay for power switching [20 usec]
D16 [sec]	0.000200000	Delay for homospoil/gradient recovery
DELTA3 [sec]	0.00201973	DELTA3=p16+d16+d0*2-p1*2/PI+de+dw*2*I30+4u
DS	16	4
in0 [sec]	0.00640000	= dw*I31
L30	4	Number of complex points at the beginning not to be included
L31	64	Number of complex points along the acquisition dimension per block
NS	128	1 * n, total number of scans: NS * TD0
TAU [sec]	0.00320000	TAU=dw*I31/2
TDav	0	Number of averages in nD

Figure S1. PSYCHE, standard acquisition parameters.

AGVIII-82-1C 5001 1 C:\Bruker\TopSpin3.2\data\HM-2020\nmr

Spectrum ProcPars **AcquPars** Title PulseProg Peaks Integrals Sample Structure Plot Fid Acqu

Probe: CryoProbe

General
Channel f1
Gradient channel

Channel f1

TAU [sec]	0.00320000	TAU=dw*131/2
TDav	0	Number of averages in nD
SFO1 [MHz]	500.1323518	Frequency of ch. 1
O1 [Hz, ppm]	2351.82	4.702 Frequency of ch. 1
NUC1	1H	Nucleus for channel 1
CNST60	10000.0000000	Sweepwidth of single chirp element in Crp_psychic.20 [10000 Hz]
CNST61	20.0000000	Desired flip angle (ca. 20 degree)
cnst62	64.150032	GammaB1/2PI value for p49 sp37 (in Hz)
cnst63	90005.281250	Scaling factor for power (sp37)
P1 [µsec]	12.990	F1 channel - 90 degree high power pulse
P44 [µsec]	240.000	F1 channel - 180 degree shaped pulse for refocussing
P49 [µsec]	30000.000	F1 channel - 180 degree shaped pulse for psychic element [30 msec]
PLW1 [W, dB]	6	-7.78 F1 channel - power level for pulse (default)
P_in [µsec]	3897.11	P_in = 1000000.0 / (cnst62*4)
SPNAM 30	Bip720,50,20,1	File name for SP30
SPOAL30	0.500	Phase alignment of freq. offset in SP30
SPOFFS30 [Hz]	0	Offset frequency for SP30
SPW30 [W, -dBW]	1.1249	-0.51 F1 channel - shaped pulse 180 degree (Bip720,50,20,1)
SPNAM 37	Crp_psychic.20	File name for SP37
SPOAL37	0.500	Phase alignment of freq. offset in SP37
SPOFFS37 [Hz]	0	Offset frequency for SP37
spw37 [W, -dBW]	6.6663e-005	41.76 spw37=plw1/cnst63
Gradient channel		
GPNAME 0	RECT.1	RECT.1
GPZ0 [%]	2.00	1%
GPNAME 1	SMSQ10,100	SMSQ10,100
GPZ1 [%]	19.00	19%
P16 [µsec]	1000.000	Homospoil/gradient pulse

Figure S2. PSYCHE, standard acquisition parameters.

1 AGVIII-82-1C 5001 1 C:\Bruker\TopSpin3.2\data\HM-2020\nmr

Spectrum ProcPars **AcquPars** Title PulseProg Peaks Integrals Sample Structure Plot Fid Acqu

Probe: CryoProbe

Experiment Width Receiver Nucleus Durations Power Program Probe Lists NUS Wobble Lock Automation Miscellaneous User Routing

Experiment

PULPROG reset_psychic_1d E Current pulse program

AQ_mod DQD Acquisition mode

FnTYPE traditional(planes) nD acquisition mode for 3D etc.

FnMODE QF Acquisition mode for 2D, 3D etc.

TD 4096 32 Size of fid

DS 16 Number of dummy scans

NS 128 Number of scans

TD0 1 Loop count for 'td0'

TDav 0 Average loop counter for nD experiments

Width

SW [ppm] 9.9974 1.2497 Spectral width

SWH [Hz] 5000.000 625.000 Spectral width

IN_F [μsec] 1600.00 Increment for delay

AQ [sec] 0.4096000 0.0256000 Acquisition time

FIDRES [Hz] 2.441406 39.062500 Fid resolution

FW [Hz] 4032000.000 Filter width

Figure S3. PSYCHE, standard acquisition parameters.

2 AGVIII-82-1C 10023 1 C:\Bruker\TopSpin3.2\data\HM-2020\nmr

Spectrum ProcPars **AcquPars** Title PulseProg Peaks Integrals Sample Structure Plot Fid Acqu

Reference Window Phase Baseline Fourier Integration Peak Deconvolution Automation Miscellaneous User

Reference

SI 16384 Size of real spectrum

SF [MHz] 500.1299614 Spectrometer frequency

OFFSET [ppm] 9.77823 Low field limit of spectrum

SR [Hz] -38.56 Spectrum reference frequency

HZpPT [Hz] 0.305176 Spectral resolution

SPECTYP UNDEFINED Type of spectrum e.g. COSY, HMQC, ...

Window function

WDW SINE Window functions for trf, xfb, ...

LB [Hz] 0.30 Line broadening for em

GB 0.1 Gaussian max. position for gm, 0<GB<1

SSB 2 Sine bell shift SSB (0,1,2,...)

TM1 0.1 Left limit for tm 0<TM1<1

TM2 0.9 Right limit for tm 0<TM2<1

Figure S4. PSYCHE and SAPPHIRE-PSYCHE, standard processing parameters.

1 AGVIII-82-1C 5000 1 C:\Bruker\TopSpin3.2\data\HM-2020\nmr

Spectrum ProcPars **AcquPars** Title PulseProg Peaks Integrals Sample Structure Plot Fid Acqu

Probe: CryoProbe

General
Channel f1
Gradient channel

General

PULPROG	sapphire_PSYCHE	Pulse program for acquisition
TD	4096	Time domain size
SWH [Hz, ppm]	5000.00	9.99735
AQ [sec]	0.4096000	Sweep width
RG	22.6	Acquisition time
DW [μsec]	100.000	Receiver gain
DE [μsec]	15.00	Dwell time
CNST4	4.0000000	Pre-scan-delay
cnst5	5.0000000	Number of points to drop when collecting FID
D1 [sec]	2.000000000	(td2/2)+1
D2 [sec]	0.014000000	Relaxation delay; 1-5 * T1
D16 [sec]	0.000200000	Delay to keep the T2 weighting constant between the pure shift
d30 [sec]	0.00640855	Gradient stabilisation delay
d40 [sec]	0.00480855	d30=in0/2
DS	16	d40=in0/2-in10
in0 [sec]	0.01281710	8, number of dummy scans
in10 [sec]	0.00160000	1/(2 * sw1)
INF1 [μsec]	25634.20	1/sw2
INF2 [μsec]	1600.00	Increment for F1
I0	0	Increment for F2
I8	0	Loop counter for F1 dimension
NS	16	Loop counter for F2 dimension
TDav	0	8 * n, total number of scans
I0orig	0	Number of averages in nD
I8orig	0	I0orig=I0
tauA [sec]	0	I8orig=I8
tauAA [sec]	0.00640855	tauA=0
tauB [sec]	0.01308000	tauAA=inf1/4
tauBB [sec]	0.01148000	tauB=d2-p17-2*d16-20u
		tauBB=d2-p17-2*d16-20u-inf2

Figure S5. SAPPHERE-PSYCHE, standard acquisition parameters.

1 AGVIII-82-1C 5000 1 C:\Bruker\TopSpin3.2\data\HM-2020\nmr

Spectrum ProcPars **AcquPars** Title PulseProg Peaks Integrals Sample Structure Plot Fid Acqu

Probe: CryoProbe

General	SFO1 [MHz]	500.1323518	Frequency of ch. 1
Channel f1	O1 [Hz, ppm]	2351.82 4.702	Frequency of ch. 1
Gradient channel	NUC1	1H Edit...	Nucleus for channel 1
	CNST20	20.0000000	Desired flip angle for PSYCHE pulse element (degree) (normally 10-25)
	CNST21	10000.0000000	Bandwidth of each chirp in PSYCHE pulse element (Hz) (normally 10000)
	cnst31	90005.281250	$cnst31 = (p30/p1) * (p30/p1)$
	cnst50	64.150032	$cnst50 = (cnst20/360) * \sqrt{(2 * cnst21) / (p40/2000000)}$
	P1 [μsec]	12.990	High power 90 pulse width
	p2 [μsec]	25.98	High power 180 pulse width
	p30 [μsec]	3897.11	$p30 = 1000000.0 / (cnst50 * 4)$
	P40 [μsec]	30000.000	Duration of double-chirp PSYCHE pulse element
	PLW0 [W, dB]	0 1000.00	Zero power (0W)
	PLW1 [W, dB]	6 -7.78	Power level for pulse (default)
	SPNAM 40	PSYCHE_Saltire_10kHz_30m E	File name for PSYCHE pulse element
	SPOAL40	0.500	Phase alignment of freq. offset in SP40
	SPOFFS40 [Hz]	0	Offset frequency for SP40
	spw40 [W, -dBW]	6.6663e-005 41.76	Power level of ZS selective pulse
Gradient channel			
	GPNAM 1	SINE.100 E	SINE.100
	GPZ1 [%]	77.00	CTP gradient [77%]
	GPNAM 2	SINE.100 E	SINE.100
	GPZ2 [%]	49.00	CTP gradient [49%]
	GPNAM 3	SINE.100 E	SINE.100
	GPZ3 [%]	63.00	CTP gradient [63%]
	GPNAM 10	RECT.1 E	RECT.1
	GPZ10 [%]	2.00	Weak gradient during PSYCHE element (1-4%)
	p10 [μsec]	30000.00	Duration of weak gradient during PSYCHE pulse element
	P16 [μsec]	500.000	CTP gradient pulse width
	P17 [μsec]	500.000	CTP gradient pulse width
	P18 [μsec]	500.000	CTP gradient pulse width

Figure S6. SAPPHIRE-PSYCHE, standard acquisition parameters.

1 AGVIII-82-1C 5000 1 C:\Bruker\TopSpin3.2\data\HM-2020\nmr

Spectrum ProcPars **AcquPars** Title PulseProg Peaks Integrals Sample Structure Plot Fid Acqu

Probe: CryoProbe

	F3	F2	F1	Frequency axis
Experiment	Experiment			
PULPROG	sapphire_PSYCHE E			Current pulse program
AQ_mod	DQD			Acquisition mode
FnTYPE	traditional(planes)			nD acquisition mode for 3D etc.
FnMODE		QF	QF	Acquisition mode for 2D, 3D etc.
ProjAngle [degree]		0		Angle for projection-spectroscopy
TD	4096	8	33	Size of fid
DS	16			Number of dummy scans
NS	16			Number of scans
TD0	1			Loop count for 'td0'
TDav	0			Average loop counter for nD experiments
Width				
SW [ppm]	9.9974	1.2497	0.0780	Spectral width
SWH [Hz]	5000.000	625.000	39.010	Spectral width
IN_F [μsec]		1600.00	25634.24	Increment for delay
AQ [sec]	0.4096000	0.0064000	0.4229650	Acquisition time
FIDRES [Hz]	2.441406	156.250000	2.364262	Fid resolution
FW [Hz]	4032000.000			Filter width

Figure S7. SAPPHIRE-PSYCHE, standard acquisition parameters.

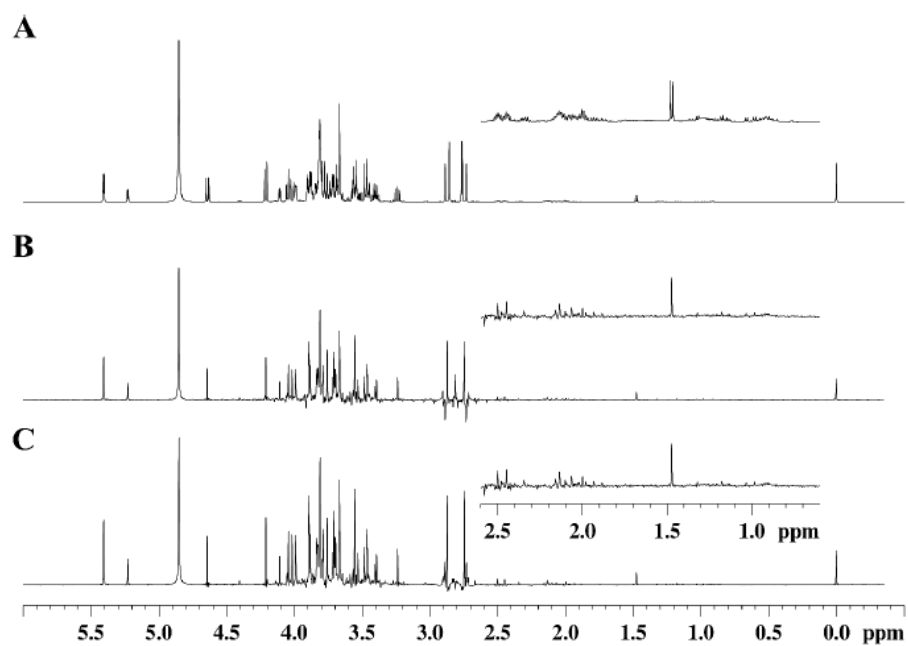


Figure S8. Representative (A) ^1H NMR, (B) PSYCHE, and (C) SAPHIRE-PSYCHE spectra of an aqueous extract of Cape gooseberries (*Bambamarca l*)

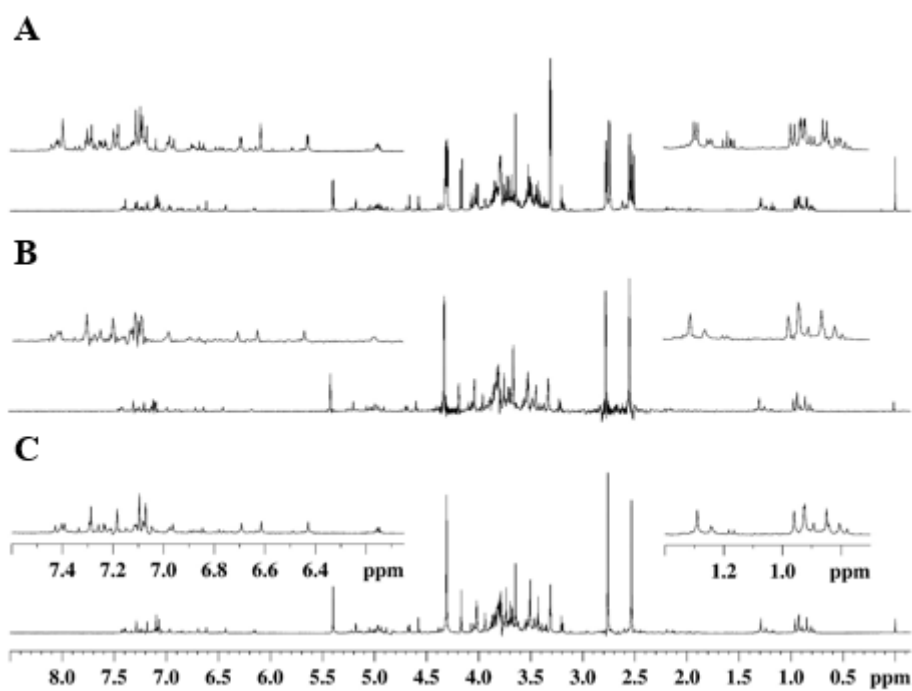


Figure S9. Representative (A) ^1H NMR, (B) PSYCHE, and (C) SAPPHIRE-PSYCHE spectra of *Vanilla pompona* extracts.

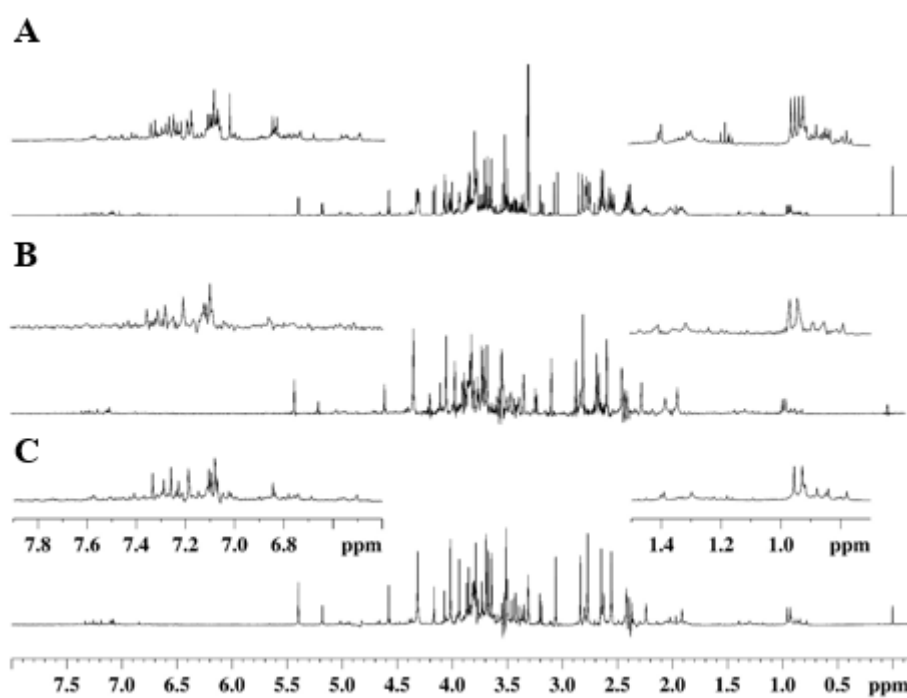


Figure S10. Representative (A) ^1H NMR, (B) PSYCHE, and (C) SAPPHERE-PSYCHE spectra of *Vanilla planifolia* extracts.

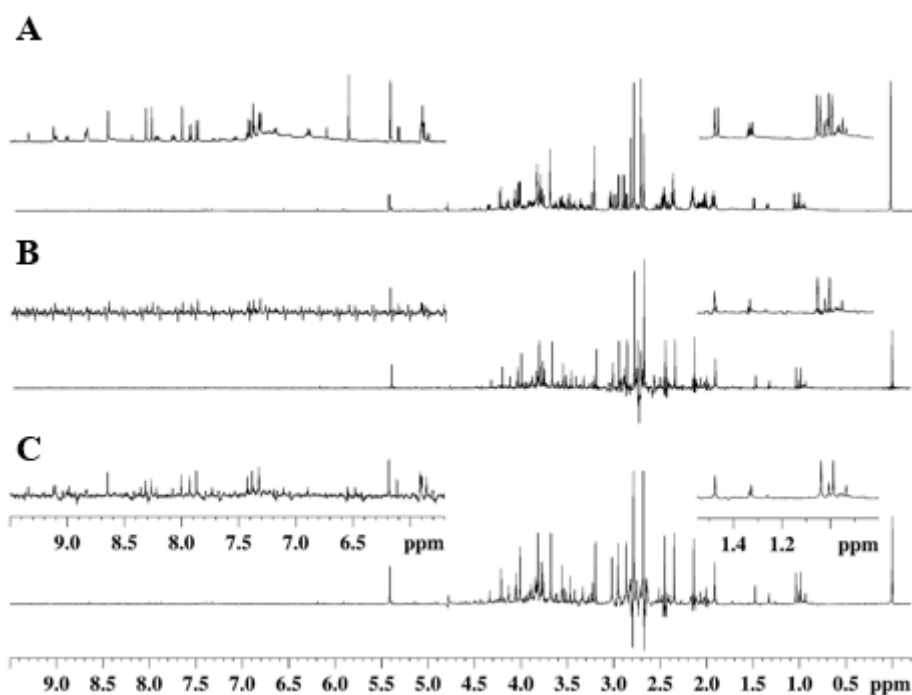


Figure S11. Representative (A) ^1H NMR, (B) PSYCHE, and (C) SAPHIRE-PSYCHE spectra of an aqueous extract of potato.

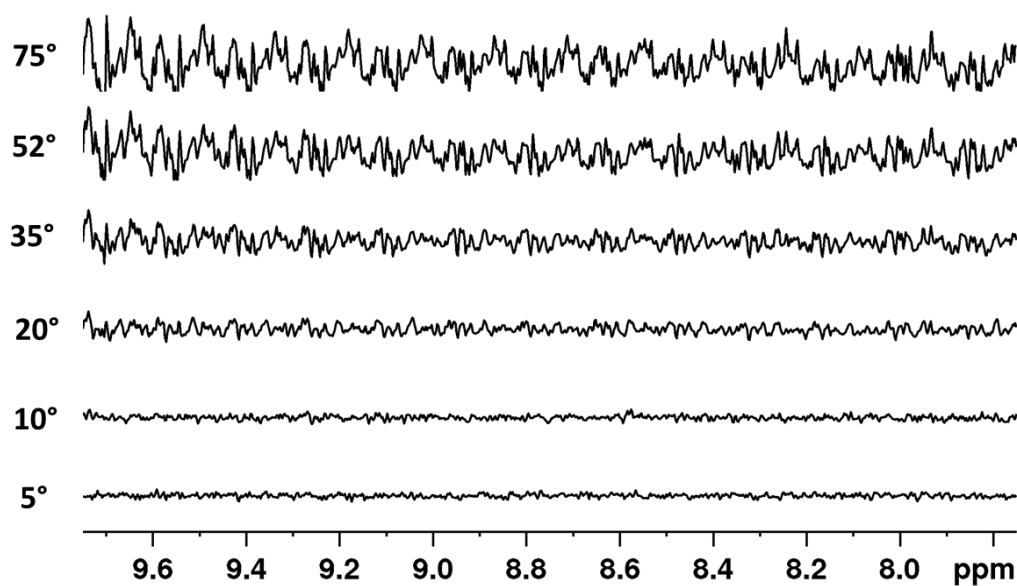


Figure S12. Expanded noise region (from 7.75 ppm to 9.75 ppm) for different PSYCHE spectra of *Vanilla planifolia* extracts using different CHIRP pulse flip angles for the PSYCHE element.